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DEHYDRATION OF $CuSO_4 \cdot 5H_2O$ STUDIED BY CONVENTIONAL AND ADVANCED THERMAL ANALYSIS TECHNIQUES

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ABSTRACT

With the aim of determining the exact dehydration (decomposition) temperatures for hydrated copper sulphate, measurements have been performed using two techniques: STA (simultaneous DTA and TG) using dynamic heating at various heating rates and SIA (stepwise isothermal analysis). In accordance with literature data, the dynamic heating measurements showed that the dehydration takes place in three steps: loss of two water molecules at 65 ° C, loss of two more at 90 ° C and loss of the final water molecule at 220 ° C. A better resolution was obtained with the SIA technique, however, which showed the following five steps: loss of one water molecule at 58 and 65 ° C, respectively, loss of $1\frac{1}{2}$ molecules at 75 ° C, loss of half a molecule at 85 ° C and finally loss of the last molecule at 215 ° C. The decomposition temperatures obtained by this technique are believed to be the most accurate data so far determined for this compound.

INTRODUCTION

Since the conception of thermal analysis techniques many measurements have been performed in order to determine the dehydration temperatures of $CuSO_4 \cdot 5H_2O$; in fact thermograms recorded for this substance are often used to demonstrate the accuracy of a given technique or apparatus. The dehydration temperatures quoted in the thermal analysis literature, for this compound as well as for other hydrates, are not consistent, however, indicating that the outcome of measurements on these compounds depends strongly on the experimental conditions applied, i.e. on the sample holder (geometry, material), heating rate, atmosphere and general technique used. The main reason for this, of course, is that dehydrations in many cases are reversible reactions which depend on the water vapour pressure of the surrounding atmosphere. Measurements in closed crucibles or in labyrinth crucibles, as used by Paulik and Paulik [1], will thus retard the dehydration

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considerably and the dehydration temperatures determined under these conditions will generally be too high.

A general question is, of course, how we define the dehydration temperature for these reversible reactions. Clearly, from the point of view of the solid, the relevant dehydration temperature is that at which the thermal vibrations of the bonds becomes large enough for these bonds to break. In the authors' opinion, the most accurate dehydration temperatures for hydrated compounds will therefore be those determined under conditions at which the influence of the released water molecules is negligible, i.e. where the water molecules are removed from the sample as soon as they are released from the solid. This may be done, for instance, by taking measurements in vacuum, by the use of plate-type sample holders, or under conditions at which the presence of water molecules in the sample holder does not affect the measurement, as is the case with the stepwise isothermal analysis (SIA) technique developed by Sørensen [2] where the temperature is maintained at the reaction temperature as long as the reaction (dehydration) proceeds. In the present work the dehydration temperature defined in this way will be termed the "decomposition temperature" in order to distinguish it from what could be termed the "equilibrium dehydration temperature", which depends on the water vapour pressure in the surrounding atmosphere.

Considering a typical TG or DTA thermogram for a dehydration reaction, what will now be the most accurate decomposition temperature? If the measurement has been performed in a cylindrical crucible, as is usually the case, then the onset (or extrapolated onset) temperature will obviously be the only temperature at which the influence of the released water is negligible. In the present work this temperature is therefore considered to represent the decomposition temperature as defined above, in contrast, for instance, with the DTA peak temperature, which is often quoted in the literature as the dehydration temperature but which more correctly represents the temperature at which the reaction is completed.

With the aim of determining the correct decomposition temperatures for $CuSO_4 \cdot 5H_2O$ measurements were performed in the present work using two techniques: STA (simultaneous TG and DTA) using dynamic heating at various heating rates, and the more advanced SIA technique, which can now be performed with a microprocessor system based on a personal computer [3,4].

LITERATURE DATA

From previous studies by Reisman and Karlak [5], Borchardt and Daniels [6] and Wendlandt [7] it was concluded that dehydration of $CuSO_4 \cdot 5H_2O$

takes place in three steps:

$$CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4 \cdot 3H_2O(s) + 2H_2O(l);\ 2H_2O(l) \rightarrow 2H_2O(g) \quad (1)$$

$$CuSO_4 \cdot 3H_2O(s) \rightarrow CuSO_4 \cdot H_2O(s) + 2H_2O(g) \quad (2)$$

$$CuSO_4 \cdot H_2O(s) \rightarrow CuSO_4(s) + H_2O(g) \quad (3)$$

Some recent data on the onset temperatures observed for these reactions by Wendlandt, who found peak temperatures in good agreement with those reported by Reisman and Karlak but slightly lower than those reported by Borchard and Daniels, as well as data reported by Paulik and Paulik and by Sørensen are given in Table 1. The literature data reported in Table 1 indicate that resolution of reactions (1) and (2) into separate steps can only be achieved in dynamic measurements using either a low heating rate or a special multiplate sample holder. In all measurements involving dynamic heating, however, a considerable overlap between the DTA and TG curves for these reactions was generally observed and this technique is thus not suitable for exact quantitative evaluation of the two reactions separately. To obtain this separation special techniques such as the constant reaction rate technique (Q-TG: Paulik and Paulik) and the SIA technique (Sørensen) are apparently necessary.

Comparing the data reported by Wendlandt [7] and Sørensen [2], there seems to be good agreement between the decomposition (onset) temperatures for reactions (1) and (2). Somewhat higher temperatures were observed, however, by Paulik and Paulik, who used the Q-TG technique. This is probably due to the higher water vapour pressure build up in the labyrinth crucible that they used for these measurements, which would retard the reactions.

Based on literature data the most accurate decomposition temperatures for $CuSO_4 \cdot 5H_2O$ are therefore believed to be:

reaction (1), loss of first two H_2O molecules at 60–65 °C;
reaction (2), loss of second two H_2O molecules at 95 °C;
reaction (3), loss of fifth H_2O molecule at 220 °C.

EXPERIMENTAL

Material: Measurements were performed on $CuSO_4 \cdot 5H_2O$ supplied by EL-NASR Pharmaceutical Chemicals, Egypt.

STA: The conventional dynamic heating measurements were carried out using a simultaneous micro thermogravimetric and differential thermoanalyzer (model DTG-30, Shimadzu, Japan). For these measurements, which were carried out in open cylindrical aluminium crucibles of 6 mm diameter and 2.5 mm height, the heating rate was varied between 1 and 20 °C min^{-1}.

TABLE 1

Some literature data on the onset (decomposition) temperatures for dehydration of $CuSO_4 \cdot 5H_2O$

Technique	Onset temperatures observed (°C)		Reference
	Peak 1		
DTA (+EGA) Crucibles; cylindrial, open, inconel dynamic heating (0.2°C min^{-1}); He atmosphere	Onset temp.	~ 60	Wendlandt [7]
	Peak temp.	85	
	Reaction (1)		
	Peak 2		
	Onset temp.	~ 95	
	Peak temp.	115	
	Reaction (2)		
	Peak 3		
	Onset temp.	~ 200	
	Peak temp.	~ 230	
	Reaction (3)		
STA Crucibles: cylindrial, open; dynamic heating; air	DTA curve		Paulik and Paulik [8]
	Peak 1		
	Onset temp.	~ 25	
	Peak temp.	150	
	Reactions (1) and (2)		
	Peak 2		
	Onset temp.	~ 230	
	Peak temp.	260	
	Reaction 3		
	TG curve		
	Onset temp.	~ 70	
	Max. rate	150	
	Reactions (1) and (2) (slight indication of two steps)		
	Onset temp.	~ 240	
	Max. rate	260	
	Reaction (3)		
STA Multiplate sampleholder dynamic heating; air	DTA curve		Paulik and Paulik [8]
	Peak 1		
	Onset temp.	~ 25	
	Peak temp.	70	
	Reaction (1)		
	Peak 2		
	Onset temp.	~ 95	
	Peak temp.	110	
	Reaction (2)		
	Peak 3		
	Onset temp.	~ 220	
	Peak temp.	230	
	Reaction (3)		

TABLE 1 (continued)

Technique	Onset temperatures observed (°C)		Reference
	TG curve		
	Onset temp.	~ 50	
	Max. rate	70	
	Reaction (1)		
	Onset temp.	~ 95	
	Max. rate	110	
	Reaction (2)		
	Onset temp.	~ 210	
	Max. rate	230	
	Reaction (3)		
Q-TG [a] labyrinth crucible; heating/cooling to maintain/constant reaction rate; air	Reaction temp. Reaction (1)	105	Paulik and Paulik [1]
	Reaction temp. Reaction (2)	115	
	Reaction temp. Reaction (3)	265–280	
SIA [b] open cylindrical crucible; temperature maintained constant during reactions; air	Reaction temp. Reaction (1)	65	Sørensen [2]
	Reaction temp. Reaction (2)	95	
	Third reaction not examined		

[a] Quasi-isothermal, quasi-isobaric; thermogravimetry.

[b] Previously Sørensen termed this technique QIA (quasi-isothermal analysis).

SIA: The SIA measurements were performed using the fully computer controlled thermogravimetric system developed at Risø National Laboratory, Denmark. The details of this system have been described previously [2–4] but briefly this system operates in the following way. As in conventional thermogravimetry, the sample is heated at a constant heating rate (in this work 1°C $\min^{-1}$) until the rate of weight change exceeds a preset limit. When this happens heating is stopped and the reaction takes place at constant temperature until the rate of weight change becomes smaller than a second preset limit, after which heating is resumed. In these measurements this second limit was chosen as one-tenth of the first limit in order to ensure completion of the reaction. Each reaction will thus take place at a characteristic reaction temperature and with this system it should be possible to differentiate between different reactions with very similar reaction temperatures. For these measurements open cylindrical alumina crucibles were used.

RESULTS AND DISCUSSION

Figure 1 shows the TG and DTA curves obtained using dynamic heating at different heating rates. In accordance with previous results these curves also show that improved resolution is obtained with decreasing heating rate and in order to separate reactions (1) and (2) completely a heating rate of 1° C min or smaller is necessary. From the curves obtained at 1° C min the following decomposition (onset) temperatures were observed:

reaction (1), 65° C;
reaction (2), 90° C;
reaction (3), 220° C.

These temperatures correspond very closely with those deduced from the literature data.

Figure 2 shows the weight versus temperature curves obtained using the SIA technique. For the removal of the first four water molecules, which by dynamic heating was observed to take place in two consecutive steps as discussed above, the SIA technique is capable of separating this reaction into four steps corresponding to loss of one water molecule at 58 and 65° C respectively, loss of $1\frac{1}{2}$ molecules at 75° C and finally loss of the last half molecule at 85° C. This technique is thus a very powerful tool for studies of reactions with reaction temperatures which lie close together. The reason for the improved resolution of the SIA technique in its present version (compare with data given in Table 1) is probably the greater sensitivity obtained with the computer controlled system—in the previous system relays operated by

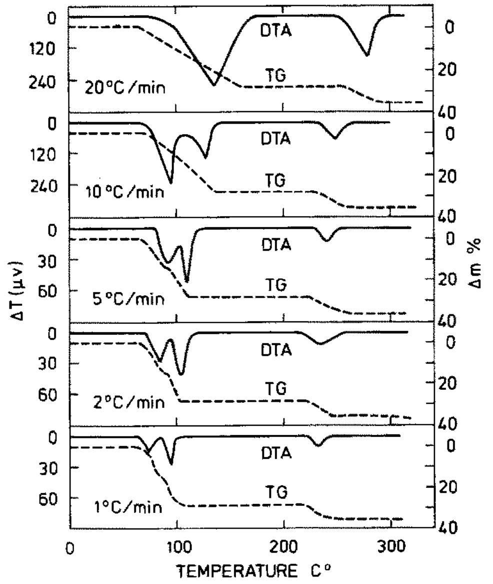

Fig. 1. TG and DTA curves obtained at different heating rates.

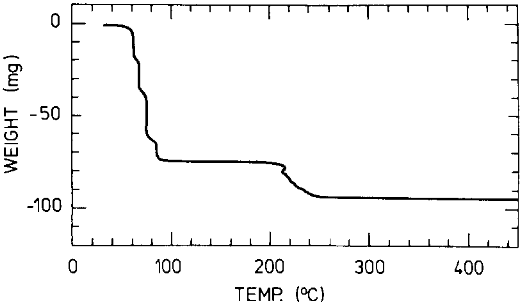

Fig. 2. SIA curve.

the DTG signal were used—and the option of using a smaller preset rate limit when the reaction is finished than when it is first detected by the system, which ensures that a given reaction is properly completed before the system resumes heating for the next reaction.

Finally, using this technique dehydration of the fifth water molecule is observed to start at 215 °C, but, in contrast with the dehydrations at lower temperatures, this reaction takes place over several smaller steps spanning a considerable temperature range (215–240 °C). The reason for this is not believed to be the occurrence of many single reaction steps but rather that this reaction is very slow and strongly temperature dependent.

CONCLUSIONS

In accordance with previous literature data STA measurements using dynamic heating have showed that proper separation of the steps involved in the dehydration of $CuSO_4 \cdot 5H_2O$ can only be achieved at a heating rate of 1 °C min^{-1} or lower. The decomposition temperatures, which in this work are defined as those at which dehydration takes place without the influence of the released water molecules and which are considered to be the true decomposition temperatures, were found by these measurements to be:

reaction (1), loss of first two water molecules at 65 °C;
reaction (2), loss of two more water molecules at 90 °C;
reaction (3), loss of fifth water molecule at 220 °C.

These decomposition temperatures correspond well with those reported by Wendlandt [7] and Sørensen [2].

Using an improved version of the SIA technique developed by Sørensen [2], even better separation of the reactions involved in the dehydration of this compound could be obtained. According to these measurements the loss of the first four water molecules can be separated into four steps corresponding to: removal of one water molecule at 58 and 65 °C, respectively; removal of $1\frac{1}{2}$ molecules at 75 °C and finally removal of the last half molecule at 85 ° C. This technique is thus very powerful for studies of reactions with very similar reaction temperatures. The removal of the fifth molecule was found by this technique to take place in the temperature range 215–240 ° C, indicating that this reaction is slow and very temperature dependent. The decomposition temperatures obtained by this technique are believed to be the most accurate data so far determined for this compound.

REFERENCES

1 F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23–59.
2 O.T. Sørensen, Thermochim. Acta, 50 (1981) 163–175.
3 O.T. Sørensen, Thermochim. Acta, 85 (1985) 287–290.
4 P.L. Husum and O.T. Sørensen, Thermochim. Acta, 114 (1987) 131–138.
5 A. Reisman and J. Karlak, J. Am. Chem. Soc., 80 (1958) 6500.
6 H.J. Borchardt and F. Daniels, J. Phys. Chem., 61 (1957) 917.
7 W.W. Wendlandt, Anal. Chim. Acta, 27 (1962) 309–314.
8 F. Paulik and J. Paulik, Hung. Sci. Instrum., 38 (1976) 17–24.